ON THE ORIGIN OF LOW FREQUENCY RAMAN LINES IN PARA-DICHLORO BENZENE.*

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Plate XVI

ABSTRACT. The Raman spectra of the two types of the crystals of para-dichlorobenzene have been reinvestigated at different temperatures. One of the types was obtained by slowly cooling the melt (Type I) and a new line at 17 cm^{-1} was observed in the spectrogram of this sample at 45°C. Another sample was prepared by suddenly cooling the melt (Type II) and at 28°C it yielded lines at 17, 40, 50 and 84 cm^{-1}, but when this sample was once cooled below 0°C and brought back to 28°C the line at 17 cm^{-1} was found to split up into two lines at 13 and 27 cm^{-1}, and the lines at 40 and 50 cm^{-1} combined to form a broad band at 52 cm^{-1}. All the six lines in the low-frequency region were found to shift away from the Rayleigh line with the lowering of the temperature up to −180°C.

It is pointed out that the different sets of lines in the low-frequency region observed in the case of the two types is due to cooling of one of the crystals once down to a few degrees above 0°C and the change is irreversible. It is further pointed out that the single crystal, which was studied by Saksena (1950), corresponds to the latter type mentioned above and the crystal in its life history might have been cooled down to a temperature a few degrees above 0°C.

The origin of these lines is discussed. The changes observed in the intensities and positions of the Raman lines due to intramolecular oscillations with solidification of the substance are also discussed.

INTRODUCTION

The Raman spectrum of para-dichlorobenzene in the solid state was studied previously by a large number of workers. Vuks (1936) first observed that para-dichlorobenzene in the solid state (not cooled below 35°C) yields a set of new Raman lines in the low-frequency region and at temperatures below 35°C, the number and position of these lines change. Sirkar and Gupta (1936), studied the Raman spectra of this crystal at different temperatures, going down up to −180°C. They observed three new lines at 40, 50, 82 cm^{-1} in the case of the crystals both at 45°C and 32°C. But these lines shifted to 46, 50, 92 cm^{-1} respectively when the crystal was once cooled in ice and again brought to about 32°C, and this change did not take place on merely cooling the crystal to a temperature just below 35°C. At −180°C, these lines were found to shift away from the Rayleigh line. Recently,

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Narain and Saksena (1951) have reported the results of investigation on the Raman spectra of two types of crystals of para-dichlorobenzene, one of which is assumed by them to be a single crystal and the other a poly-crystalline mass. They have concluded that as these two types yield two different sets of Raman lines in the low-frequency region, the structures of the two types are not probably the same. They have, however, overlooked the fact observed by Sirkar and Gupta (1936,1937) that the latter authors also observed two different sets of lines for the two types of the solid, one of which had once been cooled in ice and the other had not been cooled in that way, and that the X-ray investigation showed identical structure for two types of the solid. Saksena (1950) has also suggested that in the type of the crystal which does not yield the line 27 cm^{-1}, the molecule is rotating freely about an axis perpendicular to its plane, in the crystal lattice. Recently, an improved experimental arrangement was developed in this laboratory for studying the Raman spectra of organic crystals at different low temperatures (Bishui, 1948) and it was thought worthwhile to study the Raman spectra of the crystal of para-dichlorobenzene at different low temperatures to test the hypotheses put forward by previous workers regarding the origin of the lines in the low-frequency region.

EXPERIMENTAL

Para-dichlorobenzene, from May and Baker's original sealed bottles, was used for the present investigation. It was first crystallised out from a chemically pure benzene solution. The crystals were then melted under vacuum in a pyrex flask to which the container of pyrex glass used for the experimental observation was joined and the liquid was distilled in vacuum in the container which itself was kept at a temperature above 53°C (melting point for para-dichlorobenzene). This process was repeated a number of times. The sealed container with the final distillate was put in a heater provided with two windows at right angles to each other and the temperature inside the heater was slowly lowered to 45°C. The Raman spectra of the clear homogeneous crystal formed at this temperature, was studied with a Fuess glass spectrograph, as usual. Another sample was distilled in vacuum and condensed in a second pyrex tube, but the molten mass was solidified quickly, and cooled to about 28°C. The solid mass obtained in this way was not a single crystal and it was full of cracks. This type will be called Type II in the present paper. The Raman spectrum of this sample was first photographed at room temperature (28°C). The tube containing the crystal was held vertically in a transparent Dewar vessel and the Raman spectra of this sample at about −180°C and −100°C were next studied. The sample was again brought to a temperature of 28°C and its Raman spectrum was again photographed. The Raman spectrum of the substance in the liquid state at 60°C was also studied to test the purity of the substance. Each spectrogram contained also an iron-arc comparison.

RESULTS AND DISCUSSION

The results are given in Table I. In Table II, the frequency-shifts of the Raman lines in the low-frequency region have been compared with those observed by previous workers. Some of the spectrograms are reproduced in Plate XVI, figures 1—3. The low-frequency region enlarged about six times is reproduced in figures 4—7.

(*a*) LINES IN THE LOW-FREQUENCY REGION

From Table II it is evident that besides the three lines reported by Sirkar and Gupta (1936), a new line at 17 cm^{-1} is observed in the case of the crystal at 45°C. The line is found to persist even when the crystal is cooled down to 28°C But when the crystal is once cooled in liquid air and brought back to 28°C, an entirely different set of five lines at 13, 27, 52, 94 and 127 cm^{-1} is observed in place of the lines at 17, 40, 50, 83 cm^{-1} observed in the case of the crystal not cooled below 28°C. It appears that the line 17 cm^{-1} splits up into two lines at 13 and 27 cm^{-1} and the lines at 40 and 50 cm^{-1} combine to form a broad line at 52 cm^{-1}. The line 83 cm^{-1} shifts to 94 cm^{-1} and a new feeble line appears at 127 cm^{-1}. Neither the line 17 cm^{-1} observed in the case of the first type of the crystal nor the lines at 13 and 27 cm^{-1} observed in the case of the crystal of Type II were observed by Sirkar and Gupta (1936), probably because the quality of the spectral lines produced by the spectrograph used by them was not as good as in the present investigation. The fact, however, that on once cooling the crystal to about 0°C and again bringing it back to 32°C, a different set of lines was observed by them, is corroborated by the results obtained in the present investigation. It is also found in the present investigation that on merely cooling down the crystal of Type I from 45°C and without allowing the crystal any time to come below 28°C, no change occurs in the positions of the lines in the low-frequency region. This also confirms the observation made by Sirkar and Gupta (1936).

The results obtained by Venkateswaran (1938) also seem to corroborate the fact observed previously by Sirkar and Gupta (1936) and in the present investigation that on merely cooling down the crystal from 45°C to 25°C no change in the position of the lines takes place ; because at 25°C he observed a broad band at 48 cm^{-1} which may be assumed to represent the two lines at 43 and 55 cm^{-1} observed by him at 45°C. The frequency-shift of the other line observed by him at 25°C seems to be too high. The value ought to be 83 cm^{-1} instead of 88 cm^{-1}. He, however, did not investigate the Raman spectra of the crystal after cooling it down once to about 0°C.

Recently, Narain and Saksena (1951) have reported that they have observed two different sets of lines in low-frequency region for the first time in the case of two types of crystals of *p*-$C_6H_4Cl_2$. They have stated that they have observed in the case of a single crystal of *p*-$C_6H_4Cl_2$ prepared by

slow cooling, three new lines at 27, 54, 94 cm^{-1}, and in the case of a solid mass obtained by suddenly cooling the melt they observed these lines at 45, 57 and 84 cm^{-1}. It can be seen from Table II that the latter set of lines corresponds to the three of the four lines observed in the present investigation in the case of the crystal obtained by cooling the molten mass very slowly (Type I) up to 45°C. This crystal was absolutely homogeneous and

TABLE I

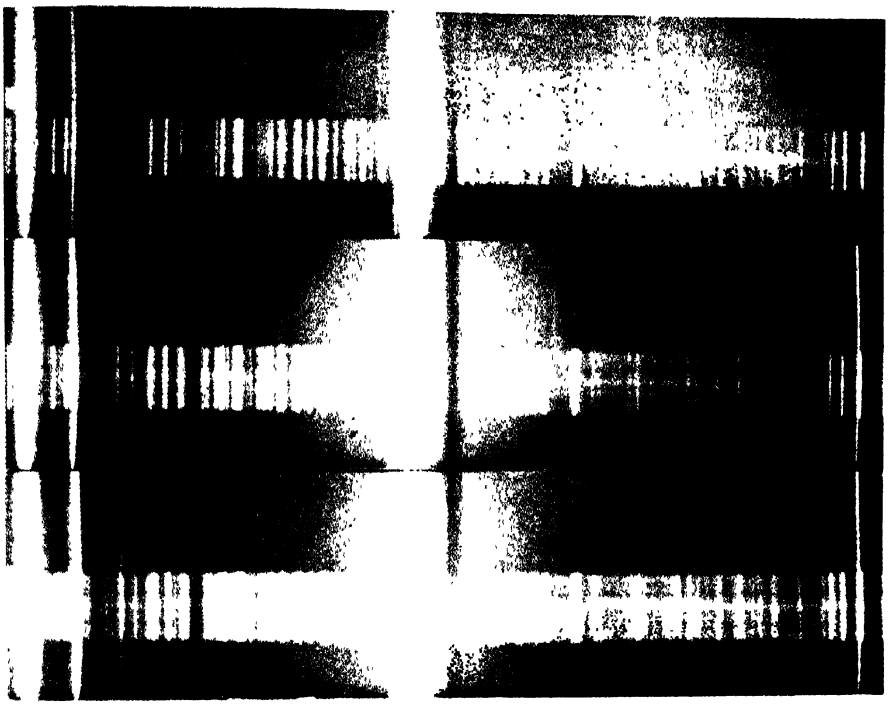
Para-dichloro-benzene ($C_6H_4Cl_2$)

Melt at 60°C $\Delta\nu$ in cm^{-1}	Crystal at 45°C $\Delta\nu$ in cm^{-1}	Crystal at 28°C $\Delta\nu$ in cm^{-1}	Crystal once cooled in liquid air		
			Crystal at 28°C $\Delta\nu$ in cm^{-1}	Crystal at about −100°C. $\Delta\nu$ in cm^{-1}	Crystal at about −180°C. $\Delta\nu$ in cm^{-1}
			13(3)e,k	11(3),k	11(3) k
	17(3),k	17(3),k	27(4)e,k	29(4)e,k	30(4)e,k
	40(2)e,k	40(2)e,k	52(4b)e,k	53(3)e,k	55(3)e.i,k
	50(2)e,k	50(2)e,k		58(5s)e,k	61(4s)e,k
	83(2b)e,k	83(2b)e,k	94(2b)e,k	102(3b)e,k	106(3s)e,k
			127(1)e,k	127(1)e,k	127(0)e,k
296(4)e,k,	306(4)e k	306(4)e k	308(4)e,k	308(4)e k	308(4)e,k
331(6)e,k,	331(6)e,k	331(6)e,k	328(6)e,k	328(6)e,k	328(6)e,k
630(2)e,k,	630(2)e,k	630(2)e,k	631(4)e,k	632(4)e,k	633(4)e,k
675(0)e,k,					
747(5)e,k,	747(5)e,k	747(5)e,k	746(5)e,k	746(5)e,k	746(5)e,k
1062(2)k,	1056(2) k	1056(2)k	1064(2)k	1072(2)k	1072(2)k
1086(1)e,k,	1086(0),e		1086(0),e	1086(0),e	1086(0),e
1109(5)e,k,	1109(7)e,k	1109(7)e,k	1109(7)e,k	1110(7)e,k	1110( )e,k
1170(0)k,			1170 0)e,k	1170(0),k	1170(0),k
1383(ob)e,k,	1383(ob)e,k	1383(ob)e,k	1383(ob)e,k	1383(os)e,k	1384(os)e k
1489(0)e,k,			1489(0)e,k	1489(0)e,k	1489(0s)e,k
1573(7)e,k,	1573(2)e.k	1573(2)e,k	1573(2)e,k	1573(2)e,k	1573(2)e,k
3068(10dd)k,	3072(10dd)k	3072(10dd)k	3072(4)k	3072(4s)k	3072(4s)k
			3076(6)k	3076(6s)k	3076(6s)k

Fig. 1.

Fig. 2.

Fig. 3



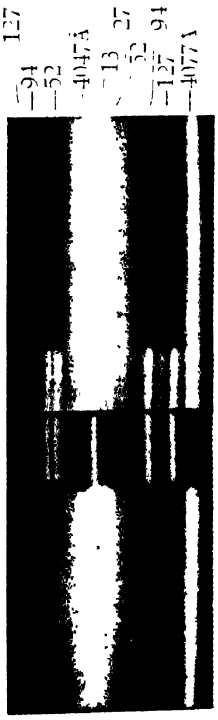


Fig. 4

Fig. 5.

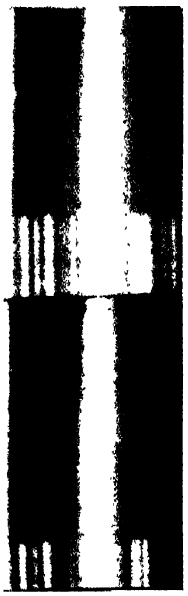


Fig. 6.

Fig. 7

Raman spectra of para-dichlorobenzene

Fig. 1 $p\text{-}C_6H_4Cl_2$ liquid at 60°C.
Fig. 2. - Do solid (once cooled in liqu'd oxygen) at 28°C.
Fig. 3. - Do solid at about—180°C.
Fig. 4. - Do solid (once cooled below 0°C.) at 28°C.
Fig. 5. - Do solid (not cooled below 45°C.) at 45°C.
Fig. 6. - Do solid at abuot—180°C
Fig. 7. - Do solid at about—100°C.

TABLE II

Low-frequency Raman lines in para-dichlorobenzene.

Sirkar and Gupta (1936)				Venkateswaran (1938)		Korshunov (1950)	Narain and Saksena (1951)		Present author				
Solid at 45°C	Solid at 32°C	Solid (once cooled in ice) at 32°C	Solid at about −180°C	Solid at 25°C	Solid at 45°C		Solid I	Solid II	Crystal at 45°C	Crystal at 28°C	Crystal once cooled in liquid air		
											at 28°C	at about −100°C	at about −180°C
$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}	$\Delta\nu$ in cm^{-1}
						8(2)					13(3)	11(3)	11(3)
						17(2)			17(3)	17(3)			
						27.5(10)	27(15)				27(4)	29(4)	30(4)
						35(2)							
40(2)	40(2)	46(2)	55(2)	48(6)	43(6)	47.5(10)		45(12)	40(2)	40(2)		53(3)	55(3)
						48.7(10)					52(4b)		
50(2)	50(2)	50(2)	60(2)		55(5)	56(10)	54(30)	57(8)	50(2)	50(2)		58(5s)	61(4s)
						72(1)							
82(2bd)	82(bd)	92(2d)	105(2s)	89(5b)	88(5b)	93(6)	94(8)	84(5)	83(2b)	83(2b)	94(2b)	102(3b)	106(3s)
											127(1)	127(1)	127(0)

approached in structure a single crystal. The lines in the low-frequency region due to such a single crystal are identical with those due to a poly-crystalline mass (not cooled up to 0°C) observed by Narain and Saksena (1951). Only the line at 17 cm^{-1} which is rather faint was not observed by the latter authors. On the other hand, the three lines observed by them in the case of their crystal of Type I, which was assumed to be a single crystal by them, agree with the three of the lines observed in the present investigation in the case of a poly-crystalline mass which had been once cooled down to a temperature below 0°C. Hence the hypothesis put forward by Saksena (1950) that the line 27 cm^{-1} is a characteristic of a single crystal and that the lines 27, 54, 94 cm^{-1} are produced in such a single crystal, while the other set of the Raman lines in the region is produced by the disoriented crystal is contradicted by the results obtained in the present investigation. The change in the positions of these lines occur only when the crystal is cooled down to about 0°C and hence the specimen assumed by Saksena (1950) to be a single crystal, must have been cooled down to a few degrees above 0°C during winter, although he has not stated it in the history of the crystal given by him. It is also seen that the line at 27 cm^{-1} is not exactly a new line characteristic of Type II of the present investigation, because the broad line observed at 17 cm^{-1} in the case of the crystal not cooled any time to 0°C splits up into two lines at 13 and 27 cm^{-1} on once cooling the crystal to about 0°C. As it has been shown by Sirkar and Gupta (1937) that no change takes place in the crystal structure of *p*-dichlorobenzene on cooling the single crystal once to about 0°C and bringing it back to about 32°C, the changes mentioned above cannot be due to any change in the lattice. So the suggestion made by Saksena (1950) that the structure of the single crystal used by him is different from that of the other type obtained by suddenly cooling the molten mass is not based on any experimental fact.

The new lines were attributed to association of the molecules in the lattice by Sirkar and Gupta (1936). According to the hypothesis put forward by Kastler and Rousset (1941) and Bhagavantam (1941) these lines are due to angular oscillations of the molecules pivoted in the crystal lattice. As pointed out in previous papers (Sirkar and Ray, 1950; Ray, 1950, 1951) these two hypotheses can be tested by studying the influence of temperature on the crystals on the number, position and intensities of the lines in the low-frequency region. Rousset (1948) assumed the line 27 cm^{-1} to be due to asymmetric angular oscillation of the pair of molecules in the unit cell of the lattice about an axis perpendicular to the plane of the molecule and a symmetric mode of this type yields a line at 47.5 cm^{-1}. The antisymmetric mode of oscillation of the pair of molecules about an axis in the plane of the molecule and perpendicular to the line joining the C—Cl line is assumed to yield a line at 47.5 cm^{-1}. The symmetric mode of the latter oscillation is assumed to give a line at 56 cm^{-1}. In the present investigation, however, the crystal once cooled in liquid oxygen and brought back to 28°C has

yielded five lines at 13, 27, 52, 94 and 127 cm^{-1}. The line at 52 cm^{-1} is a broad band which splits up into two lines at 53 and 58 cm^{-1} at $-100°C$. The lines at 13 and 27 cm^{-1} are very sharp and they shift very slightly in opposite directions on lowering the temperature of the crystal to $-180°C$. Hence Rousset's assignment cannot be assumed to be correct, because the line at 27 cm^{-1} is connected intimately with the line at 13 cm^{-1} as both originate from the line 17 cm^{-1}. Further, if the lines were due to angular oscillations of the molecules in the Vander Waals' field in the lattice, such wide separation of the lines due to symmetric and anti-symmetric modes of oscillation would not have taken place. In fact, such a separation would indicate strong coupling between the two molecules in the unit cell. Also, the value of the frequency, especially that of the line at 94 cm^{-1} would indicate a large value of the force of restitution which is hundred times larger than the Vander Waals' forces even if the oscillation is assumed to be an angular one, as pointed out by Sirkar (1951). Further, the frequencies of the four lines observed at 28°C cannot be explained by taking into account the appropriate moments of inertia of the molecule about its three axes and assuming the value of ν to be given by the equation

$$\nu^2 = \frac{\beta}{4\pi^2 I}$$

It has previously been pointed out by the present author (Ray, 1951) that the positions of some of the new lines in the low-frequency region in some substituted benzene compounds do not depend on the moments of inertia of the molecules. The intensities of the lines in the low-frequency region do not seem to diminish appreciably when the crystal of para-dichloro-benzene is cooled down to $-180°C$. Hence these results, as well as those obtained in the previous investigations do not support the theory put forward by Kastler and Rousset (1941) and by Bhagavantam (1941) that the lines are due to angular oscillations of the molecules in the Vander Waals' field in the lattice.

Recently, Korshunov (1950) has reported 9 new lines at 8, 17, 27.5, 35, 47.5, 48.7, 56, 72 and 93 cm^{-1} in the case of one modification of p-$C_6H_4Cl_2$ and he has assigned six of these lines to rotational oscillations and three (*viz.*, 8, 17 and 35 cm^{-1}) to the translational oscillation. He has stated that the non-ideality of the crystal has allowed the latter three forbidden oscillations in the Raman effect. These results are not in quite agreement with those observed in the present investigation, because the type which yields the line 27.5 cm^{-1} does not yield the line 17 cm^{-1}. There is, of course, a line at 13 cm^{-1} which is rather sharp. As regards the lines at 8, 35 and 72 cm^{-1} the spectrograms obtained in the present investigation did not record them. On the other hand, there is an extra line at 127 cm^{-1}. The presence of the line at 8 cm^{-1} could not be detected in the present investigation, because the spectrograph itself produces a line in this position. The postulate that non-ideality of the crystal is responsible for the appearance

of forbidden lines is rather vague, because the nature of non-ideality is not specified, and the difficulties in explaining the origin of the other six lines mentioned above are present in the explanation offered by Korshunov. The postulate given by Sirkar and Gupta (1936) that virtual bonds between neighbouring molecules alter the polarisability of the pair of molecules during oscillation against each other is more specific and all the properties of the lines in the low-frequency region can be explained on this hypothesis.

(*b*) *Intramolecular oscillations.* As regards the frequency-shifts of the lines due to intramolecular oscillations, the changes observed with the solidification of the melt are not remarkable, excepting that the line at 296 cm^{-1} shifts to 306 cm^{-1} on solidifying the melt. But when the substance is once cooled in liquid oxygen and again brought back to 28°C the lines at 306 cm^{-1} and 331 cm^{-1} shift respectively to 308 and 328 cm^{-1}. This change is the same as that observed by Sirkar and Gupta (1936) on cooling the crystal once in ice and bringing it back to 32°C. The line at 3068 cm^{-1} shifts to the higher wave-length side and splits up into two components at 3072 and 3076 cm^{-1} respectively, when the melt is solidified and is further cooled down up to −180°C.

The frequencies of the lines due to C-Cl and C=C valence oscillations are not found to be affected much with the lowering of temperature up to −180°C. It is evident that the asymmetry in the lattice field is responsible for the splitting up of the symmetric C-H oscillation into two components at −180°C.

Although the positions of the other lines due to intramolecular oscillations remain the same with the solidification of the substance, the intensities of two of these lines undergo remarkable changes. It can be seen from Table I as well as from figures 1—4, Plate XVI, that the intensity of the line 1573 cm^{-1} due to the liquid is larger than that of the line 1109 cm^{-1}, but in the case of the solid the line at 1573 cm^{-1} is much feebler than the line at 1109 cm^{-1}. Again the lines 1109 cm^{-1} and 747 cm^{-1} have almost the same intensity in the case of the liquid while in the case of the solid the former line becomes more intense. As the line 1573 cm^{-1} can be attributed to the presence of C=C bond in the ring, it appears that the number of such bonds in the molecule in the solid state is smaller than that in the liquid state. If this assumption be true, it leads to the conclusion that probably in the case of this compound having a benzene ring in the molecule, association takes place in the solid through one of the C=C bonds. Such a hypothesis has, however, to be tested only by studying the Raman spectra of other similar molecules.

The sharpness of all the prominent Raman lines at 28°C and their further sharpening at lower temperatures in the present investigation indicate that the scattering is incoherent and is actually due to the oscillations in the individual molecule in the unit cell. That the probability of the simultaneous

occurrence of the same mode of oscillation for all the molecules in the unit cell is less than that for random oscillations, has been pointed out by Sirkar and Ray (1950) and the results obtained in the present investigation also corroborate such a view.

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